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Discussion on the challenges of DMFC catalyst loading process for mass production

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Abstract

In manufacturing direct methanol fuel cells, there are two critical processes: manufacturing the membrane-electrode assembly, and loading the catalyst. The catalyst loading process is especially influential on the efficiency of the DMFC. In this paper, we focus on the catalyst loading process for mass production capabilities. The study focuses on evaluating the application of screen printing machinery to catalyst loading. This is approached by discussing different methods of catalyst deposition, considering their loading range, equipment used, ink form, base substance, and ink contents. Then an empirical study of screen printing machinery is concluded. The study concludes that the screen printing method is the most suitable way of loading the catalysts in the case of scale-up.

Keywords: Direct methanol fuel cell; Catalyst loading; Screen printing; Spray; Spreading; Painting

1. Introduction

Direct methanol fuel cells (DMFCs) are an alternative for the current metal-based batteries in portable electronics [1–3]. If the theoretical advantages of DMFCs are achieved, simultaneously with cost reductions, the technology could be widely adopted in different applications. In the technology's current state, researchers are producing one sample or few samples at a time. Scale-up of the manufacturing process is hardly discussed in the literature.

In manufacturing DMFCs, there are two critical steps: the MEA fabrication and the catalyst loading. Concerning the latter, several methods have been developed, such as spreading, spraying, sputtering,

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painting, screen-printing, decaling, electrodeposition, evaporative deposition, and impregnation reduction [1]. Methodological chaos related to loading processes increases the confusion about which of the methods would be the most applicable to a specific requirement. Most of the research has used a doctor blade or airbrush [3, 6–18] to perform the loading of the catalyst. Even though several researchers have compared different catalyst loading methods [4, 5], discussion on why a specific catalyst loading process is used is, however, scarce.

In this paper, the research is focused on the screen-printing method used for DMFC catalyst loading. Screen-printing is seen to be a practical method in MEA manufacturing as it has several advantages, such as reproducibility, easy procedures, and economic catalyst usage for mass production [19]. Several authors [20, 21] have also studied the effects of different methods. However, although showing that screen-printing is a practical manufacturing method, Hwang et al. [22] reported that screen-printing produced cracking, which inhibited the performance of the MEA produced with this method. The present study reviews the plausible methods used for MEA assembly from a mass manufacturing point of view, and reports on the step-by-step procedure involved in catalyst loading with screen printing.

2. The comparative study of different loading methods

2.1. Overview of loading methods' effectiveness for mass production

In theory, the fabrication of a DMFC MEA is not a complicated process. It includes two steps: catalyst loading and layer assembly. In the deposition process, the catalyst can be loaded either onto the gas diffusion layer (GDL), or onto the membrane. It has been suggested that using the catalyst-coated membrane (CCM) method makes a good contact between the catalyst layer and the electrolyte membrane, which can effectively reduce the catalyst loading without sacrificing cell performance [23]. Hu et al. [44] also claim that the CCM method increases performance, since it obtains better conductivity. However, the CCM method is limited by membrane swelling and wrinkling problems, which could cause serious damage to the catalyst layer. The loading should be a subtle process, or the membrane will need pre-treatment. For example, high-temperature loading is a possible solution. Controlled solvent removal processes can also help [33]. However, no matter which substance is loaded, the primary challenge in the assembly of MEAs is to achieve good contact between the membrane, GDL, and catalyst layers. Good contact maximises catalyst utilisation during the cell's operation, which has a clear impact on efficiency.

In addition to focusing on the base substance, the catalyst ink content is a complex question. Suzuki et al. [24] has shown that using 30 wt% ionomer in the catalyst offers the best performance. Liu et al. [25] has reviewed several papers, and suggested that carbon should be added to the platinum catalyst to increase its efficiency. Lim et al. [26] argues that the best utilisation of the catalyst is a metal loading of 0.5–0.7 mg/cm^2 with the carbon-supported Pt-Ru catalysts in the anode; further increasing the loading does not have a positive effect on the power performance. However, different studies always use their own specific catalyst content proportions. Also, the raw materials used are supplied by different suppliers. This makes the analysis of catalyst ink content much more complex. In addition, the catalyst ink used in the processes is in different forms, such as liquid/suspension form [27], paste/slurry [28], and even directly using a dry metal [29], which make comparisons even harder to make.

As mentioned, the loading process includes several different methods, which also adds to the difficulty of making comparisons. While some of them are commonly used, such as spreading or spraying, others are rarely reported on. Methods such as evaporative deposition and impregnation

reduction have been reported only in a few papers [30]. In addition, some of the studies [31] mix different processes, such as using electro- and air spraying simultaneously, or using sputtering on the anode side and spraying on the cathode side.

Since there are several methods with several ink types, ink contents, and base substance without any certain solution, it is difficult to determine if one loading method is better than another. In this paper, the aim is to find a method suitable for mass production. The productivity, stability, applicability, and coefficient of utilisation are used as evaluation criteria.

2.2. Different loading methods

Spraying usually refers to a process that uses an airbrush to load the catalyst ink. It could be a manual or an automatic process. To the authors' knowledge, there are no articles using an automatic spraying process; however, machinery for this has been made available.

In the process, a liquid ink is often used. Even though a slurry ink has been suggested [42], most of the inks used for spraying are in the form of a liquid/suspension. In the process, the loading period should be neither too fast, which will cause the layer to be uneven or flooded, nor too slow, which will cause the catalyst ink to settle down and agglomeration. There is a detailed example described by Jörissen et al. [32] on the challenges of the spraying method.

The loading amount in a spraying process is usually in the range from 0.1 to 2 mg/cm^2. The minimum loading amount is said to be 0.1 mg/cm^2, since a loading lower than 0.1 mg/cm^2 usually leads to poor DMFC performance. The loading amount is controlled by weighing the difference between before and after the spraying, which is time-consuming. If the CCM system is applied, the membrane also needs a pre-treatment period. The spraying process should be implemented in portions, to avoid sedimentation during the processing. Since each operation and measuring process is time-consuming, spraying is not suitable for a high catalyst loading. However, some researchers have obtained a large catalyst loading by spraying. For example, Lee et al. [42] obtained an 8 mg/cm^2 catalyst loading by spraying. In that study the equipment used was not mentioned, but the ink was in a slurry form.

Spreading refers to loading the catalyst layer by using a doctor blade or a similar instrument. During the process, the slurry/paste is dropped or squeezed to the surface of the GDL or membrane. Then the surface is smoothed using automated or hand tools, to ensure a uniform catalyst layer. Park et al. [23] exemplified the process whereby a slurry form catalyst is used.

The loading amount obtained by the spreading method is usually more than 1 mg/cm^2. The loading is controlled by the thickness or weight of the layer produced. Limited by the equipment used, the thickness of the catalyst layer cannot be too thin. It is difficult to create a uniform surface or low catalyst amounts.

Painting refers to a process where the loading is performed using a brush or a roller. Mao et al. [34] described experiments in using the painting method. The method is based on dipping the brush into the catalyst suspension/slurry, then running it on the GDL surface. The printing process usually loads the catalyst on the surface of the GDL instead of the membrane, because the GDL has a rough surface, which it is easy for the catalyst to attach to. There are some exceptions, such as Gottesfeld and Wilson [43], who described a process where a layer of ink is painted directly onto a dry membrane and baked to dry the ink.

The loading amount with the painting process is usually more than 1 mg/cm^2. Catalyst loading is controlled in the same manner as with the spraying method, as an accurate result cannot be achieved by measuring the catalyst layer thickness. The weight of the loaded GDL, measured before and after the loading process, is the only measure of catalyst loading. However, this has a significant degree of inaccuracy.

Screen-printing is another commonly used loading method. It usually uses a paste as the deposition material, but liquid/suspension has also been suggested. Commercial screen printers are designed to hold the screen parallel to and in proximity with the substrate. A squeegee is used to provide the force necessary to force the paste through the openings onto the substrate [35]. An empirical examination of MEAs prepared by the screen-printing method has been given by Marcelo et al. [36].

The screen-printing process can handle a thin catalyst layer, starting from 0.2 mg/cm^2, which is controlled by the height or the weight of the catalyst layer. This process has a similar principle to that of the spreading method, but the screen printing process is more controllable during the loading. The method has been used in electronics manufacturing, more precisely surface-mount device (SMD) processes, and thus is commonly used at an industrial scale.

Sputtering is a momentum transfer process. In sputtering, the incident particles are usually ions, which are accelerated by an applied electrical potential [37]. If the angle and energy used are appropriate, the sputtered atoms and ions can be attached to a substrate to form a thin film. An example can be found in the work of Makino et al. [45], who used the sputtering method in fuel cell catalyst loading.

With the sputtering method, we try to achieve high catalyst utilisation. This means that the loading range of sputtering should be kept smaller than 1 mg/cm^2. The sputtering equipment controls this. Sputtering is the most accurate method of all the methods reviewed in this paper, and offers the best utilisation of catalyst [45].

A summary of the characteristics of these methods is shown in Table 1.

Table 1. Comparative study of different loading methods.

Loading method	Loading range (mg/cm^2)	Equipment	Ink form	Base substance	Ink content
Spraying	<2	Air brush	Liquid	GDL/membrane	Metal powder/with carbon/with PTFE/with ionomer
Spreading	>1	Doctor blade	Paste/slurry	GDL/membrane	With carbon/with PTFE/with ionomer
Painting	>1	Brush or roll	Liquid/paste/slurry	GDL	With carbon/with PTFE/with ionomer
Screen printing	0.2–6	Screen printing machine	Paste/slurry	GDL/membrane	With carbon/with PTFE/with ionomer
Sputtering	<1	Sputtering machine	Metal	GDL/membrane	Pure metal

2.3. Rarely used loading methods

There are some other rarely used loading methods available. In this paper, a brief introduction of these, which is an excerpt from the paper 'Review and analysis of PEM fuel cell design and manufacturing' [30], is given for reference.

Electrodeposition: Described in the work of Gottesfeld & Zawodzinski [38] and Taylor et al. [39], electrodeposition is the impregnation of the porous carbon structure with ionomer. By exchanging the cations in the ionomer with a cationic complex of platinum followed by electrodeposition of platinum onto the carbon support, this will result in deposition at the sites that are accessible by both carbon and ionomer.

Impregnation reduction: Also called electro-less deposition, this is described by several researchers [40, 41]. In this method, 'the membrane, ion exchanged to the Na^+ form, is equilibrated with an aqueous solution of $(NH_3)_4PtCl_2$ and a co-solvent of H_2O/CH_3OH' [30]. After the impregnation, 'vacuum dried PFSA in the H^+ form is exposed on one face to air and the other to an aqueous reductant $NaBH_4$' [30]. This method has been seen to produce good catalyst loadings (2–6 mg Pt/cm^2) in the structure.

Evaporative deposition: Foster et al. [40] and Fedkiw & Her [41] describe a method where (NH3)4$PtCl_2$ is evaporatively deposited onto the membrane. This is done from an aqueous solution. The process is concluded, after the evaporation, by immersing the membrane in a solution of $NaBH_4$. This immersion produces salt and metallic platinum. 'The method has been found to produce metal loadings of the order of ≤0.1 mg Pt/cm^2 on the membrane/catalyst assembly' [30].

Dry spraying: The method of Gulzow et al. [29] uses reactive materials (Pt/C, PTFE, PFSA powder and/or filler materials) which are mixed in a knife mill. The fabricated mix is then atomised and sprayed directly onto the membrane. The spraying process described to be done via 'a nitrogen stream through a slit nozzle' [30]. This method requires a hot rolling or pressing process for additional adhesion. An advantage of this method is that, depending on the degree of atomisation, a uniform reactive layer with controlled thickness can be manufactured.

Catalyst decaling: Refers to a process in which membranes are catalysed using a 'decal' process in which the ink (Pt, solubilised PFSA, and glycerol) is cast onto PTFE blanks for transfer to the membrane by hot pressing [38]. When the PTFE blank is peeled away, a thin casting layer of the catalyst is left on the membrane, followed with a rehydrated process using lightly boiling sulfuric acid and water.

2.4. Manufacturability of the methods

In the laboratory, achieving the highest performance is the critical factor. In the case of mass manufacturing, in addition to the performance, the productivity, stability, applicability, and coefficient of utilisation have to be considered.

The spraying method can tolerate a variety of different catalyst contents. Metal powder or metal attached to the carbon black, or the catalyst mixed with PTFE and ionomer, are all suitable. The method can also be applied to the automatic assembly line. However, the loading process is time-consuming. After each spraying, the ink should be remixed again, or the ink should be mixed during the spraying process, as the liquid ink agglomerates easily. During the spraying process, parts of the catalyst will

remain in the air, and parts of the catalyst will be sprayed onto the support material. The platinum lost in these two cases cannot be recovered.

In spreading and screen-printing, the catalyst loading process is fast and stable, and the catalyst layer can be formed in a single process. The paste does not need to be remixed as often as with the spraying process, but the solvent evaporation need to be considered. Both of these methods are efficient; most of the catalyst can be used and recovered. These methods also have a high impurity tolerance. However, the loading is restricted by the tools and equipment used. Some kinds of catalyst, such as Pt black, are seldom used in these methods, since the pure metal loading leads to a very thin layer, which cannot handled by these methods.

Painting methods can be utilised with all types of inks. The quality of the result relates to ink viscosity and adhesion of the membrane/GDL. However, the loading process is slow. Also, the painting process produces a significant amount of waste, as a significant amount of catalyst will remain on the brush or roller, which needs to be cleaned and recovered immediately. Pt black is seldom used in this method.

The sputtering process uses a completely different approach to the catalyst loading process. In this process, a metal ion is used for loading. Ions sputtered into the air cannot be recovered. However, the method is a significantly accurate method in its material consumption.

In this evaluation, it is assumed that the productivity, stability, applicability, and coefficient of utilisation are equally important. The best-performing method for each criterion is graded 5, and the worst-performing method is graded 1. The comparison of the common methods is shown in Fig. 1.

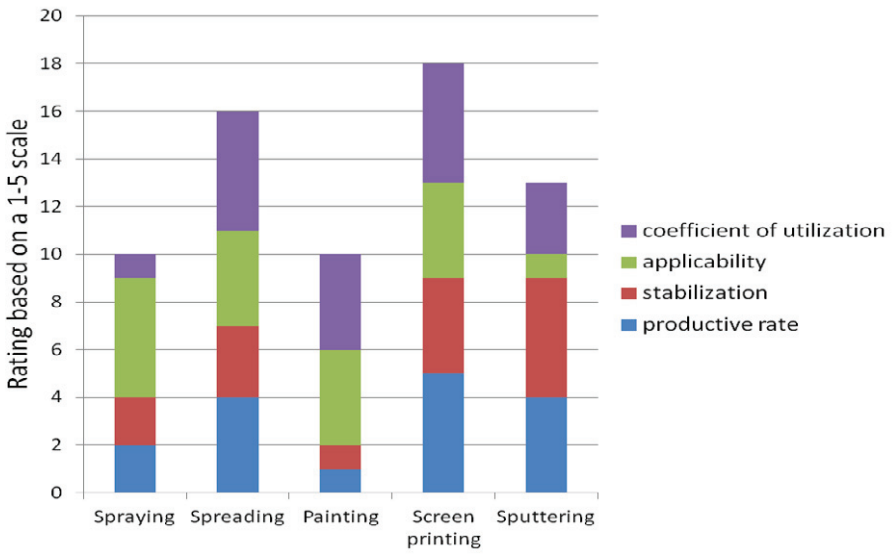

Fig. 1. Comparison of the common methods.

The loading period represents the productivity. Spraying is the slowest among the commonly used processes graded as 1, and screen printing is the fastest process graded as 5. The others fall between them.

The precision of the loading reflects to the stability. The sputtering method has the smallest loading limit graded as 5, and painting has the highest loading limit graded as 1. Applicability means how many different types of ink can be applied and how wide the loading range is. In this case, the spraying handles several different catalyst contents graded as 5; on the contrary, sputtering can only handle one type of catalyst, so has the narrowest loading range, graded as 1. The platinum catalyst is an expensive noble metal, and waste should be kept to the absolute minimum. Screen-printing and spreading (graded as 5) can recover most of the unused material; but with spraying (graded as 1) several catalysts cannot be reused.

In Fig. 1, the screen-printing method is seen as the most suitable way to load catalysts in the case of mass production. It has the shortest operation time, is stable, and can accept many different types of ink and impurities. The recovery of the waste is also easy. In addition, screen-printing is a method often used in electronics manufacturing.

3. Screen printing process

In this paper, a further study of the screen printing process has been carried out with an experiment. As mentioned, in the screen printing process, the squeegee is activated and travels across the surface of the screen, forcing the paste through the openings onto the substrate. In the experiment, a screen printing machine is used (AP25, MPM Corporation) for loading the catalyst onto the membrane. The membrane as the substrate is connected on the surface of a PCB. The catalyst ink was used as a paste, and stainless steel, with an opening of 1 cm × 1 cm, was used as a stencil.

The membrane used in this experiment is Fumapem F-14100 (dry thickness: 100–120 μm, Fumatech GmbH). This membrane was pre-treated as follows. The membrane samples were put in an aqueous 10 wt% HNO_3 solution for 12 h at t = 80°C, then treated for 1 h in distilled water at t = 80°C, and finally rinsed with distilled water. The catalyst ink was prepared by dispersing carbon supported Pt/PtRu (BASF) onto carbon black, then adding isopropanol/water (5:1) solution, with 30 wt% Fumion (FLNA-905, Fumatech GmbH). The liquid should be added drop by drop in order to keep it as a paste. Superfluous liquid in a short time may change the paste into a solution. A photograph of the loading result and the cross-section are shown in Fig. 2.

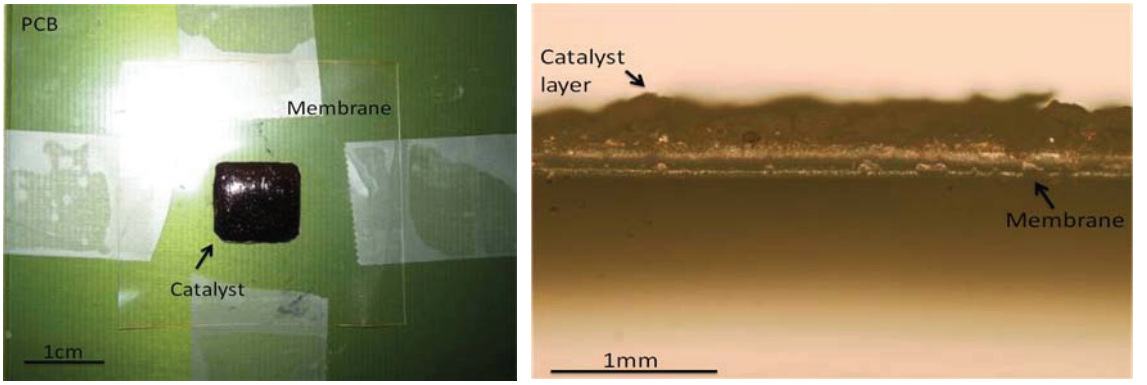

Fig. 2. Catalyst loading by screen printing equipment, and cross-section image.

The experimental result shows that the screen printing method can be applied to DMFC catalyst loading. The operation is automatic and simple. It takes a very short time; the result is stable and uniform. The unused paste was recovered after the process. It confirms the theoretical analysis above.

However, this process also holds some challenges. First, screen-printing a large area such as 1 cm × 1 cm will require the catalyst paste to have a very precise geometry, allowing complex interconnection patterns to be generated. A paste that is too dry will fracture the catalyst layer; a paste that is too wet will cause the boundary effect, which causes the edge catalyst layer to be thicker than the middle. In this case study, the silk threads are applied as a mesh on the top of the membrane, which divided the membrane into six small areas. It helped to reduce the boundary effect influence. Membrane swelling and wrinkling are also a problem. In this experiment, the paste was made as wet as possible, and we tried to make the catalyst layer as thin as possible. Even though some swelling still existed, the catalyst layer was not broken by it. The viscosity of the paste may change during printing because of solvent evaporation, which also needs to be considered. Last but not the least, because of the large number of variables involved, the optimised values for each variable should be tested case by case.

4. Conclusions

In this paper, different methods of catalyst deposition are discussed, by considering their loading range, equipment used, ink form, base substance, and ink contents. Then a comparison of the current commonly used methods is discussed. The conclusion is that the screen printing method is the most suitable way of loading the catalysts in the case of scale-up. It is based on the same equipment as used in electronics manufacturing, which makes it more suitable for mass production. Empirical work also gives the same conclusion.

In the future, scale-up experiments should be made with different loading methods, especially the screen-printing method, to try to produce multiple cells in one go. A more detailed comparison should be carried out with the experimental results.

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